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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

OKINAKA ET AL.

SERIAL NO. 10/022,801

GROUP ART UNIT: 1773

FILED: December 20, 2001

EXAMINER: H. T. LE

FOR: SPINDLE-SHAPED MAGNETIC
ALLOY PARTICLES FOR MAGNETIC
RECORDING, AND MAGNETIC
RECORDING MEDIUM

DECLARATION UNDER 37 C.F.R. 1.132

HONORABLE COMMISSIONER OF PATENTS & TRADEMARKS

WASHINGTON, D.C. 20231

SIR:

Now comes Yasutaka OTA, a citizen of Japan, and a resident of 3-10-18, Sue, Onoda-shi, Yamaguchi-ken, Japan, who declares and says that:

1. I graduated from the Department of Chemistry, Faculty of Science, Shimane University in March, 1983.

2. I am currently employed by TODA KOGYO CORPORATION since April, 1983.

3. I am familiar with the work related to U.S. Patent Application, Serial No. 10/022,801, and am a co-inventor of U.S. Patents: No. 5,156,922, No. 5,238,483, No. 5,466,306, No. 5,531,922, No. 5,599,378, No. 5,645,652, No. 5,735,969, No. 5,968,226, No. 5,989,516 and No. 6,447,618.

4. Under my control and supervision the following experiments were conducted:

Experiment 1 (Examples 1, 16 and 31 of U.S. Patent No. 5,989,516)

<Production of Goethite Particles>

20 litre of an aqueous solution containing 25 mol of Na_2CO_3 , 10 litre of an aqueous solution containing 18 mol of NaOH (molar ratio: 0.72) (equi-molar ratio: 1.70), and 0.25 atm% of water glass #3 (calculated as Si) based on the total Fe were charged in a reaction vessel which was maintained in a non-oxidizing atmosphere by introducing N_2 gas thereinto at a rate of 50 litre/minute. With the resultant aqueous solution was mixed 20 litre of an aqueous ferrous sulfate solution containing 20 mol of the total Fe (Fe^{+2} concentration: 0.4 mol/litre) at a temperature of 47°C to produce a suspension containing an Fe-containing precipitate.

The suspension containing an Fe-containing precipitate was held at 47°C for 60 minutes while continuously blowing N_2 gas thereinto at a rate of 50 litre/minute. Thereafter, an aqueous cobalt sulfate solution was added thereto so that the suspension contained 18 atm% of Co based on the total Fe, and the mixed suspension was aged for 4 hours.

Air was introduced into the aged suspension containing an Fe-containing precipitate at 47°C at a rate of 90 litre/minute, and when the oxidation fraction reached 40%, 1.75 atm% of water glass #3 (calculated as Si) based on the total Fe was added, and the oxidation was further continued for 100 minutes

under the same oxidation condition to produce yellowish brown precipitated particles. The pH of the suspension during the aeration was 8.0 to 9.5. The total oxidation time was 22 minutes.

The yellowish brown precipitated particles were filtered out, washed with water, dried and pulverized by an ordinary method to obtain about 2 kg of yellowish brown particles (spindle-shaped goethite particles).

<Production of Hematite Particles>

The amount of press-cake which was equivalent to 800 g of the spindle-shaped goethite particles obtained in the above was suspended in 15 litre of water. The pH of the suspension was 8.5.

10 wt% of aluminum nitrate nonahydrate, 7 wt% of neodymium nitrate hexahydrate, 10 wt% of cobalt acetate tetrahydrate, each based on the goethite particles, were added to the suspension. Thereafter boric acid was added to the suspension so that the content of boric acid became 15 wt% based on the goethite particles and the mixed suspension was stirred for 10 minutes. The pH of the suspension was 4.5.

After adjusting the pH of the suspension to 9.5 by adding an aqueous ammonia solution, the suspension was filtered by a filter press, washed with water and dried to obtain the goethite particles coated with Al, Nd, Co and B compounds.

The goethite particles coated with Al, Nd, Co and B compounds were dehydrated at 400°C in air so as to produce spindle-shaped hematite particles.

<Production of Spindle-shaped magnetic iron-based alloy particles>

100 g of the spindle-shaped hematite particles coated with Al, Nd, Co and B compounds obtained in the above were charged in a fixed bed reducing furnace having an inner diameter of 72 mm, and H₂ gas was introduced into the furnace at a rate of 35 litre/minute so as to reduce the particles at 420°C. The reduction process was finished when the dew point of the exhaust gas reached -30°C. The reducing time was 370 minutes.

After the end of reduction, H₂ gas was replaced with N₂ gas, and while the N₂ gas was introduced into the furnace at a rate of 50 litre/min, the hematite particles were cooled to 40°C. A mixed gas of 50 litre/min of N₂ gas and 0.2 litre/min of air was then introduced into the furnace while the furnace temperature was maintained at 40°C. After the exothermic peak produced by the oxidation with the mixed gas was observed, the air flow rate was raised to 0.4 litre/min so as to increase the air ratio in the mixed gas. In this way, the air mixing ratio was raised by stages by raising the air ratio in the mixed gas every time the exothermic peak produced by the oxidation was observed. Finally, the oxidation process was continued by a mixed gas of 0.6 litre/min of air and 50 litre/min of N₂ gas until no exothermic reaction due to oxidation was observed and the temperature of the particles became 40°C, which was approximately the same as the

temperature of the furnace. During the oxidation, the temperature of the particles reached 75°C at the maximum.

The air mixing ratio was then gradually increased while maintaining the furnace temperature at 40°C and the flow rate of N₂ gas at 50 litre/min until the amount of air was 10 litre/min. No exothermic reaction was observed during this period. Thereafter, the temperature was cooled to the room temperature while aerating with the mixed gas of N₂ gas and air under the same condition.

After the aeration was stopped and the air was replaced with N₂ gas, the spindle-shaped magnetic iron-based alloy particles containing cobalt and iron as main ingredients with an oxide layer was recovered.

As is obvious from the electron microphotograph, the spindle-shaped magnetic iron-based alloy particles had an average major axis diameter of 0.085 µm, an average minor axis diameter of 0.013 µm, and X-ray crystallite size D_{110} of 148 Å with a uniform particle size and containing no dendrites. As to the magnetic characteristics, the coercive force (H_c) was 2032 Oe, the saturation magnetization was 138 emu/g, and the squareness (σ_r/σ_s) was 0.518. The Co content in the particle was 17.94 atm% and the amount of coating Co was 2.29 atm%, the Si content in the particles was 1.93 atm%, the amount of coating Al was 2.91 atm%, the amount of coating Nd was 1.53 atm%, and the amount of coating B was 12.8 atm%.

The various properties of the obtained particles are shown in Table.

(1) The average major axis diameter, average minor axis diameter and aspect ratio of spindle-shaped goethite particles, spindle-hematite particles and spindle-shaped magnetic alloy particles are respectively expressed by averages of values measured by an electron microscope.

(2) The amounts of Co, Al, rare earth elements and other metal elements contained in spindle-shaped goethite particles, spindle-hematite particles and spindle-shaped magnetic alloy particles were measured using an inductively coupled high-frequency plasma atomic emission spectroscope (SPS-4000 Model, manufactured by Seiko Denshi Kogyo Co., Ltd.).

(3) The BET specific surface areas of the respective particles are expressed by the values measured by a BET method using "Monosorb MS-11" (manufactured by Cantachrom Co., Ltd.).

(4) The crystallite size D_{110} (X-ray crystallite size of spindle-shaped magnetic alloy particles) is expressed by the thickness of the crystallite as measured in the direction perpendicular to each crystal plane (110) of the spindle-shaped magnetic alloy particles by an X-ray diffraction method using an X-ray diffractometer manufactured by Rigaku Co., Ltd. (measuring conditions: target: Cu; X-ray tube voltage: 40 kV; X-ray tube current: 40 mA). The value was calculated on the basis of the X-ray diffraction peak curve prepared with

respect to the respective crystal planes, from the following Scherrer's formula:

$$D_{110} = K\lambda/\beta\cos\theta$$

wherein β is a true half-value width of the diffraction peak which was corrected with respect to the width of machine used (unit: radian); K is a Scherrer constant ($= 0.9$); λ is a wavelength of X-ray used (Cu $K\alpha$ -ray 0.1542 nm); and θ is a diffraction angle (corresponding to a diffraction peak of the crystal plane (110)).

(5) The magnetic properties of spindle-shaped magnetic alloy particles were measured using a vibration sample magnetometer "VSM-3S-15" (manufactured by Toei Kogyo Co., Ltd.) by applying an external magnetic field of 795.8 kA/m (10 kOe) thereto.

(6) The changing percentage ($\Delta\sigma_s$) of saturation magnetization of particles for evaluating an oxidation stability of the particles (hereinafter referred to merely "oxidation stability of saturation magnetization"), and the changing percentage (ΔB_m) of saturation magnetic flux density B_m of a magnetic coating film for evaluating a weather resistance (oxidation stability) of the coating film (hereinafter referred to merely "oxidation stability of saturation magnetic flux density"), were measured as follows.

That is, the particles and the magnetic coating film were

allowed to stand in a constant-temperature oven maintained at 60°C and a relative humidity of 90% for one week to conduct an accelerated deterioration test. Thereafter, the particles and the magnetic coating film were measured to determine the saturation magnetization value and saturation magnetic flux density, respectively. The oxidation stability of saturation magnetization ($\Delta\sigma_s$) was calculated by dividing the difference (absolute value) between the values σ_s and σ_s' measured before and after the one-week accelerated test, respectively, by the value σ_s measured before the accelerated test, and the oxidation stability of saturation magnetic flux density (ΔB_m) was calculated by dividing the difference (absolute value) between the values B_m and B_m' measured before and after the one-week accelerated test, respectively, by the value B_m measured before the accelerated test. The closer to zero the oxidation stability of saturation magnetization ($\Delta\sigma_s$) and oxidation stability of saturation magnetic flux density (ΔB_m), the more excellent the oxidation stability of the particles and the magnetic coating film.

(7) The rotational hysteresis integral value R_h and anisotropy field H_k of the spindle-shaped magnetic alloy particles were measured using a torque-type magnetometer manufactured by Digital Measurement Systems Co., Ltd. by the following method.

That is, first, demagnetized spindle-shaped magnetic alloy particles were enclosed in a capsule and applied with an external magnetic field. The external magnetic field applied to the particles was varied from 19.9 kA/m (250 Oe) to 795.8 kA/m (10 kOe) at intervals of 19.9 kA/m (250 Oe) while reciprocating a rotation angle of the magnetic field from 0° to 360° and further back to 0° at intervals of 563°, thereby measuring a hysteresis loss W_r of magnetic torque at the respective magnetic fields. The measured hysteresis loss values W_r were plotted with respect to the inverse number of the magnetic field applied ($1/H$). On the basis of the plotted curve, the rotational hysteresis integral value R_h was obtained from the following formula:

$$R_h = \int (W_r/M_s) d(1/H)$$

wherein M_s represents a saturation magnetization value (emu/cm^3).

Further, the anisotropy field H_k was determined by reading the value of a crossing point between a maximum-gradient tangent line of the W_r - $1/H$ curve drawn on a higher magnetic field side of the curve, and the axis for the inverse number of the magnetic field applied ($1/H$).

(8) The activation volume V_{act} of spindle-shaped magnetic alloy particles was measured using a vibration sample magnetometer (manufactured by Toei Kogyo Co., Ltd.) by the following method.

That is, first, spindle-shaped magnetic alloy particles were enclosed in a capsule, and magnetized by applying an

external magnetic field of 795.8 kA/m (10 kOe) thereto. Then, at 300 K, the magnetic field applied was varied along the demagnetization curve from 200 Oe to 3,600 Oe at intervals of 200 Oe, and maintained at each value to measure the change in magnetization due to thermal oscillation magnetic after-effect for 1,000 seconds. The thus measured value was determined as an amount of magnetization attenuated (ΔM). Immediately after the measurement, the magnetic field applied was increased by 200 Oe at which the amount of magnetization attenuated was similarly measured. Then, the magnetic field applied was decreased by 200 Oe to measure a reversible magnetic susceptibility χ^{rev} . The total differential magnetic susceptibility χ^{tot} was obtained by dividing a difference in magnetization value obtained when the change in magnetization with time after 1,000 seconds became small, by 200 Oe.

The irreversible magnetic susceptibility χ^{irr} in the range of 200 Oe to 3,600 Oe, was obtained by subtracting the reversible magnetic susceptibility χ^{rev} from the total differential magnetic susceptibility χ^{tot} . Since the activation volume of the spindle-shaped magnetic alloy particles showed a moderate magnetic field-dependency, the coercive force H_c was used as its typical value.

Then, the activation volume V_{act} was calculated from the following formulae (1) and (2):

$$S_v = \Delta M / (\chi^{\text{irr}} \cdot \ln t) \quad (1)$$

$$V_{\text{act}} = k_B \cdot T / M_s \cdot S_v \quad (2)$$

wherein k_B represents a Boltzmann's constant; and S_v represents a magnetic after-effect constant.

(9) The true density of the spindle-shaped magnetic alloy particles was measured by a constant-volume expansion method using a Multi-Volume Densitometer 1305 manufactured by Micro Meritecs Co., Ltd.

Table 1

	Properties of spindle-shaped magnetic alloy particles			
	Shape	Co/Fe (atm%)	Al/Fe (atm%)	Nd/Fe (atm%)
Our invention	-	20-50	-	-
Experiment 1	Spindle-shaped	20.13	2.91	1.53

Table 1 (continued)

	Properties of spindle-shaped magnetic alloy particles	
	Average major axis diameter (μm)	Average minor axis diameter (w) (μm)
Our invention	0.03-0.10	0.008-0.020
Experiment 1	0.085	0.013

Table 1 (continued)

Examples and Comparative Examples	Properties of spindle-shaped magnetic alloy particles	
	BET specific surface area value (m^2/g)	Crystallite size (D_{110}) (\AA)
Our invention	40-75	100-160
Experiment 1	60.8	148

Table 1 (continued)

Examples and Comparative Examples	Properties of spindle-shaped magnetic alloy particles	
	Activation volume (V_{act}) (μm^3)	Rotational hysteresis integral (Rh) (kA/m)
Our invention	0.01-0.07E-4	≤ 1.0
Experiment 1	0.089E-4	1.38

Table 1 (continued)

Examples and Comparative Examples	Properties of spindle-shaped magnetic alloy particles			
	Coercive force (Hc)		Saturation magnetization value (σ_s)	
	kA/m	Oe	Am ² /kg	emu/g
Our invention	159.2-238.7	2000-3000	100-150	100-150
Experiment 1	161.7	2032	138	138

Table 1 (continued)

Examples and Comparative Examples	Properties of spindle-shaped magnetic alloy particles	
	Squareness (r/s) (-)	Oxidation stability ($\Delta\sigma_s$) (%)
Our invention	0.52-0.55	≤ 15
Experiment 1	0.518	15.3

Remarks

As seen from the above, the activation volume (V_{act}), the Rotational hysteresis integral (Rh) and the squareness (σ_r/σ_s) of the spindle-shaped magnetic alloy particles of Experiment 1 (U.S. Patent No. 5,989,516) are $0.089E-4 \mu m^3$, 1.38 and 0.518 which are out of the range of our invention.

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false

statements may jeopardize the validity of the application or any patent issuing thereon.

Date: October 23, 2003


Yasutaka Ota